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by

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X-RAY PHOTOEMISSION STUDIES OF THE SURFACE COMPOSITION OF LUNAR IMPACT GLASS SAMPLES INCLUDING 12054: R. M. Housley and R. W. Grant, Rockwell International Science Center, Thousand Oaks, California 91360.

It has been known for some time now that the surfaces of lunar regolith samples are significantly enriched in heavy isotopes of O, Si, C, N, and S with respect to their parent materials. Several mechanisms including hydrogen stripping, micrometeorite vaporization, solar wind sputtering, and preferential sticking of vaporized or sputtered atoms have been suggested to account for the isotopic enrichments. These mechanisms would also lead to characteristic elemental fractionation patterns.

The surface compositions of regolith fines samples do indeed differ from their bulk compositions (1,2), but not in a way which fits with qualitative expectations for any of the above mechanisms. This led to the suggestion (1,2) that the surface compositions of impact produced glasses in the regolith might differ from their bulk compositions when they are formed. The main cause of the difference between surface and bulk compositions of lunar fines might be the agglutination process itself.

To test this hypothesis we have used x-ray photoemission spectroscopy (XPS) to measure the surface compositions of four glass coated fragments from the 1-2 mm 14161 fines.

We have also studied two samples from the unique lunar rock 12054. This is a highly shocked basalt whose top surface was almost completely coated with glass. Its orientation on the lunar surface when collected was well documented and it appears to have spent its entire surface residence, estimated to be 1-3 x 10^3 years, in this orientation (3).

Our sample 12054,68 from the upper surface is heavily microcratered and partly covered with accreta. Sample 12054,69 from a reentrant crack which apparently did not look directly out to space, shows no craters or accreta visible at 40x with a binocular microscope.

It was anticipated that comparison of data on these 12054 samples would also provide direct evidence on chemical fractionation produced by solar wind sputtering or vapor deposition.

Surface compositions for both groups of samples obtained from XPS data in the 0-200 eV binding energy range by a procedure previously described (2) are given in Table 1. For comparison, the bulk composition obtained by Wänke et al. (4) on the $\lesssim$1 mm size fraction of the same Apollo 14 fines sample, and the average composition of the 12054 glass as obtained by Schaal and Hörz from 25 microprobe analyses are also given. In the Fe row, R indicates that the Fe is moderately reduced, comparable to the state observed in bulk fines samples. WR indicates weakly reduced Fe and NR indicates no reduction. The surface compositions have been renormalized to 100 percent excluding the volatiles Na, Cl, S, P, and K.

Looking at data on the 12054,69 crack surface we see a strong Fe enrichment and moderate Mg and Ca depletions. There is also a strong surface enrichment in the volatiles Na, Cl, P, S, and K, and no Fe reduction.

On the 12054 top surface we see a very similar pattern for the nonvolatile elements with Fe enrichment and Mg and Ca depletion. The volatile elements, however, were present at much lower levels, which were not quantitatively determined. Reduction of Fe was pronounced, but somewhat less than

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that observed in mature fines samples. The only clearly evident effects of the surface exposure are the reduction of Fe and the strong depletion in volatile elements.

Turning now to the 14161 samples, the one showing no reduced Fe has significant surface P. All four show surface depletions in Al and Mg while Fe and Si are variable. No evidence for exposure induced changes in major element chemistry is apparent.

Although far from conclusive, these results lend support to the hypothesis that impact induced glass formation itself makes a major contribution to the observed differences between surface and bulk composition in lunar fines samples (1,2). The depletion in surface volatiles associated with Fe reduction suggests that at least a modest amount of sputtering accompanies solar wind implantation.

The absence of evidence for major element changes associated with vapor deposition or solar wind sputtering leaves unresolved the dominant mechanism responsible for producing the heavy isotope enrichments observed in lunar fines. However, if solar wind sputtering is important, the surface enrichments in S and K and depletions in Ca (2) produced by impact glass generation can contribute to understanding why S and K are much more highly fractionated than Ca (6).

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X-RAY PHOTOEMISSION STUDIES

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TABLE 1. Surface compositions of lunar glass samples expressed in atomic percent.

	14161 1	14161 2	14161 3	14161 4	14163 Bulk*	12054,68 Top	12054,69 Crack	12054 Bulk**
Si	17.78	20.05	18.65	18.54	18.01	15.40	16.27	16.96
Aℓ	6.18	6.88	6.66	6.45	7.96	4.41	3.14	4.39
Mg	3.65	3.44	3.66	4.16	5.15	3.26	3.43	5.39
Fe	7.22 R	3.10 R	5.17 WR	4.43 NR	3.25	13.97 R	14.06 NR	6.42
Ca	4.35	4.87	4.34	4.89	4.08	3.23	3.10	4.81
Ti	0.38	-	0.36	0.44	0.41	0.62	0.72	1.39
O	60.43	61.75	61.17	61.10	61.14	59.11	59.28	60.26
Na							1.8	0.17
Cl							0.2	
S							0.9	
P				0.7			0.3	
K							1.5	

* Wänke et al. (4)

** Schaal and Hörz (5)

SCANNING AUGER MICROPROBE AND ATOMIC ABSORPTION STUDIES OF LUNAR VOLCANIC VOLATILES:

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We report new experimental results obtained as part of our continuing effort to understand the nature, extent, and behavior of volatile phases associated with lunar volcanism. Such understanding of the behavior of volatile phases is necessary for the proper description of lunar volcanism and for the interpretation of volatile trace metal depletion in lunar basalts or enrichment in lunar fines.

We are making a new series of Auger studies of glass balls from the 15425 and 74001 fines using a recently acquired PHI model 590 scanning Auger microprobe (SAM). The electron beam in this instrument can be focused down to a diameter of 1000 Å and can be scanned to obtain an image similar to that obtained with a scanning electron microscope (SEM). Selected spectra obtained from balls in the three well identified volcanic categories (1) are shown in Fig. 1.

Initial results indicate that: 1) Volatiles, in the outer few atomic layers sampled by Auger spectroscopy, vary considerably from ball to ball, in each class, ranging from nearly unobservable low values to values giving spectra similar to those shown in Fig. 1. 2) Variability over the surface of individual balls is smaller, as long as chipped areas are avoided. 3) The dominant volatiles on balls in all three classes are S and Zn. 4) Other volatiles commonly observed are P, Cl, and K.

Although direct comparison of Auger data with SEM x-ray fluorescence data on the same spots has not yet been done, it appears from the general level of x-ray intensities reported by Butler and Meyer (2) that 5 to 10 times more S and Zn must exist in a diffuse zone $\lesssim 0.5$ μm thick than is seen in the outer few atomic layers.

Thermal release profiles of Zn and Cd obtained from individual particles and bulk samples of 74001 black glass, by flameless atomic absorption techniques (3), indicate that the major fractions of these elements reside on the surfaces of grains. This agrees with results obtained for Zn by Wasson et al. (4) using leaching experiments.

These results all support the picture of volatile transport during lunar volcanism previously outlined by Butler and Meyer (2). At the time of eruption or during the very early high temperature portion of their existence volatiles are very effectively outgassed from lunar pyroclastic glasses. Later volatiles begin to recondense on the glass balls while they are still hot enough for significant diffusion to take place. Finally, up to about a monolayer of volatiles condense after they have cooled to the point where diffusion is negligible.

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SCANNING AUGER MICROPROBE STUDIES

Cirlin E.H. and Housley R.M.

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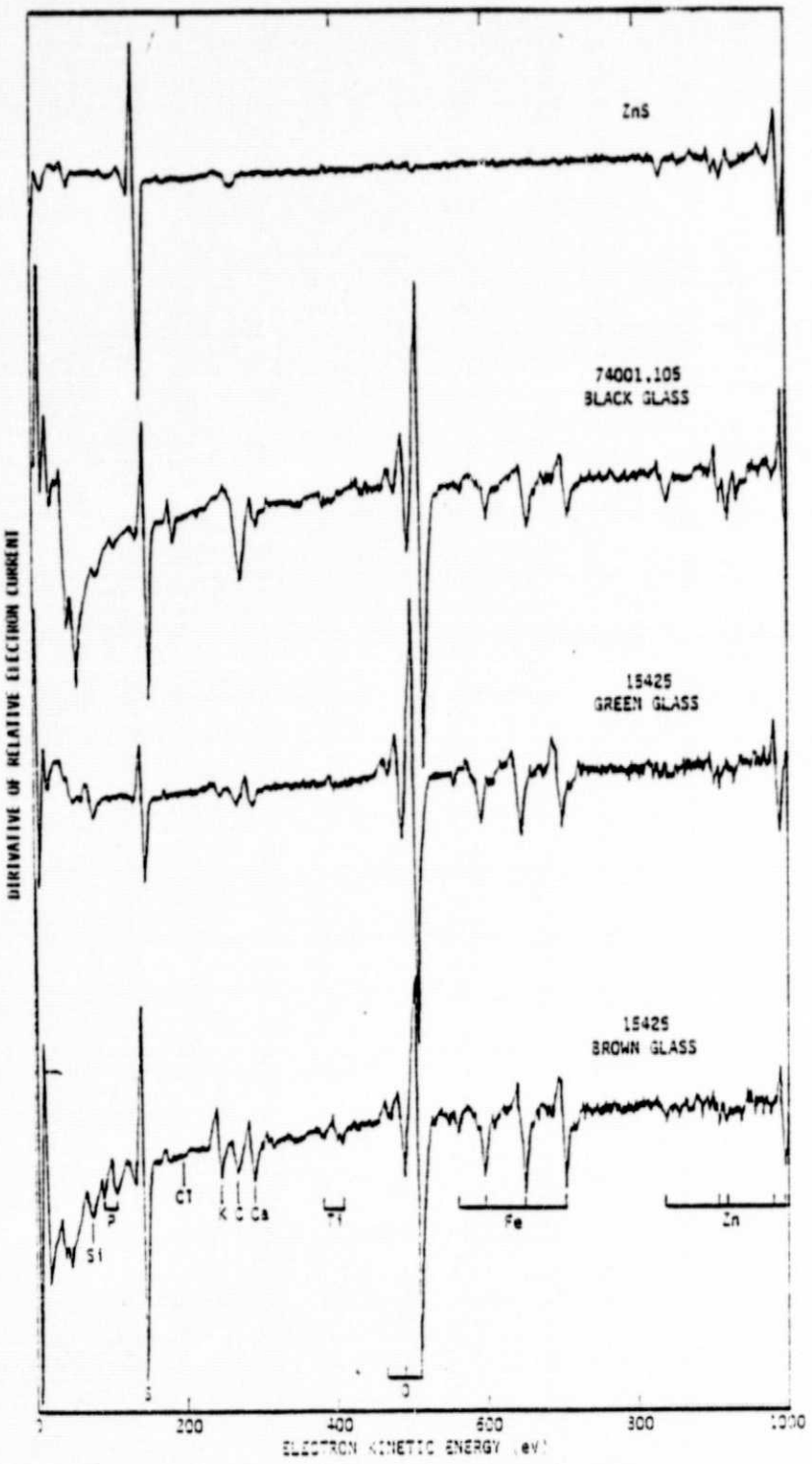

Fig. 1. Auger spectra of glass balls from the three recognized lunar volcanic pyroclastic groups. Note the volatile coatings with S and Zn predominant and P, Cl, and K sometimes important.